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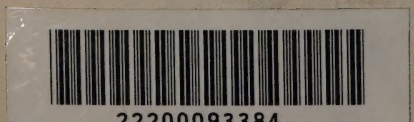
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Part iv.—The Chemistry of the Duboisias.

By James M. Petrie, D.Sc., F.I.C., Linnean Macleay Fellow of the Society in Biochemistry.

(From the Physiological Laboratory of the University of Sydney.)

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THE CHEMICAL INVESTIGATION OF SOME POISONOUS PLANTS IN THE N.O. SOLANACEÆ.

Part iv.—The Chemistry of the Duboisias.

By James M. Petrie, D.Sc., F.I.C., Linnean Macleay Fellow of the Society in Biochemistry.

(From the Physiological Laboratory of the University of Sydney.)

The genus of Australian plants known as Duboisia consists of three or possibly four species. Two of these are well known—*D. myoporoides* and *D. Hopwoodii*, and have formed the subject of numerous investigations by chemists, pharmacologists, and physicians during forty years. In regard to their active principles, they are perhaps the most interesting of all our native flora, and have received greater attention than any others The third—*D. Leichhardtii*—is a Queensland species, and nothing is known of its chemical composition or active constituents. *D. Campbelli* has been recorded as probably a new species, but apparently it has never been botanically described. It was found in Western Australia ten years ago, and since the first record appeared (Journ. W. Aust. Nat. Hist. Soc., 1906) nothing further concerning it has been made known.

Duboisia myoporoides R.Br.

i. This evergreen tree is native to Eastern Australia and the islands to the north. Its range extends from the Shoalhaven River in the south to Cape York, and is continued into New Guinea, the Philippine Islands, and New Caledonia. It was described in 1810 by R. Brown(**17**), who named the genus after the French botanist Dubois. Brown placed it in the family Solanaceæ; Bentham transferred it to Scrophulariaceæ; and when

its poisonous properties had been discovered, von Mueller replaced it among the familiar poison-plants of the Solanaceæ.

ii. It was well known to the aborigines as a poison-plant, and we have the first intimation of its powerful properties from Woolls(**18**), about 1860. "The aborigines make holes in the trunk and put some fluid in them, which when drunk on the following morning produces stupor. . . . . Branches are thrown into pools for the purpose of intoxicating the eels and bringing them to the surface. . . . . Branches hung up in a close room have had the effect of producing giddiness and vomiting."

iii. About this same time, another and somewhat similar plant had been brought back from the interior of Australia by the Burke and Wills Expedition, and this plant was described by von Mueller(**1a**) as *Anthocercis Hopwoodii* (Hopwood being the chief subscriber to this expedition). Bancroft, in 1872, obtained from travellers in the interior, specimens of a plant greatly prized by the aborigines, and which they called "pituri"; and in 1876 von Mueller and Bailey identified pituri with *Anthocercis Hopwoodii*, by the microscopic structure of the leaves. Previous to this, Bentham had doubted the position given to this plant by von Mueller, and in 1876 the latter, after receiving fruiting-specimens from the Giles Expedition(**1c**), transferred it, at Dr. Bancroft's suggestion, to the genus Duboisia.

Bancroft, having learned that pituri was used by the aborigines as a narcotic, made extracts and tried the effects on animals(**19**). His interesting results at once suggested the examination of the other species of Duboisia, which was apparently never suspected of having valuable properties. Von Mueller wrote, in 1877, that *D. myoporoides* probably shares the same properties as *D. Hopwoodii*, since both have the same burning acrid taste; and that the properties of both Duboisias will prove similar to those of stramonium.

iv. At von Mueller's suggestion, Bancroft then made watery extracts of the leaves of *D. myoporoides*, and after injecting small amounts into domestic animals, he observed that the "pupil of the eye was always widely expanded, that the animals

walked as if blind, and if let alone fell asleep"—properties quite different from those he had observed in pituri. He then tried the effect of dropping the extract into the eye of animals and also into the human eye, and again after a few minutes wide dilation was observed. Bancroft then sent some of his aqueous extracts to ophthalmic practitioners in Brisbane, Ipswich, and Sydney hospitals. By them, his observations were confirmed, and the midriatic properties were carefully studied on the human eye. The reports of their work are contained in Bancroft's paper on "Pituri and Duboisia"(**3**). Bancroft used the Duboisia regularly instead of atropia in his ophthalmic practice, and also used it in cases of asthma. The main effects observed were midriasis, confusion of intellect, thirst, and loss of taste.

v. It was in 1877 that Staiger, then Queensland Government Analyst, first prepared the active principle of *D. myoporoides*, from Bancroft's material(**6**). He found it to be "a yellow oily-looking substance, which refused to crystallise either alone or with acids, and not volatile at 212°F."

vi. At the end of 1878, Bancroft visited England, and took with him specimens of the plant and a few pounds of the extract, which he distributed among various experts for further investigation.

Ringer and Tweedie(**20**) made a detailed study of the properties of *the extract*, and of the effects on the eye. Tweedie first brought the drug before the medical world in England. Holmes (**21**) gave a general account of all the previous work before the Pharmaceutical Society, and at the discussion of the paper, Gerrard stated that "the extracts used were bad pharmaceutical preparations, having the appearance of resinous watery extracts, very acid, therefore likely to be irritating." Gerrard(**22**) afterwards prepared the active principle from the extracts supplied to him through Holmes. His method was solution in alcohol, evaporation, and removal of the alkaloid with chloroform, solution in acid water, and precipitation by ammonia. The precipitated alkaloid quickly formed heavy oily drops which were left as a yellow viscid mass. Its chemical reactions were then compared with those of atropine, and found to be different.

Drs. Ringer and Murrell(23), working with Gerrard's alkaloid, made careful experiments on its physiological action. They observed dilatation of the eye, the action on the skin in arresting perspiration, headache and drowsiness, the antagonism to muscarine, and the production of tetanus in frogs. The authors concluded, from both physiological and chemical evidence, that the alkaloid was not atropine.

Paul(24), in 1878, further examined the alkaloid prepared by Gerrard, and confirmed the latter's results.

vii. Petit, of Paris(11), in 1879, identified the alkaloid of pituri as nicotine, and also prepared the alkaloid of *D. myoporoides* from an aqueous extract of the *leaves*. In a letter to Holmes, which is included in Paul's paper, Petit pointed out the differences from atropine.

In the Lancet for 1879, eight cases of poisoning from the use of duboisia were described by Davidson(25); the symptoms were giddiness and delirium. Tweedie ascribed the cause to impurities, but he afterwards found that his own pure solutions, which he had used with Dr. Ringer, produced the same toxic symptoms.

Dr. Norris(26) found the therapeutic action similar to atropine, but more energetic. Ringer(27) also described the action as far more powerful than atropine.

viii. Baron von Mueller and Rummel(28), in January, 1879, described their preparation and the properties of "Duboisine," the alkaloid of *D. myoporoides*. They state that the alkaloid was prepared like nicotine from the leaves and twigs, that it was a *volatile*, yellow, oily liquid, lighter than water, having a strong odour of tobacco and cantharides, and probably identical with "piturine" from *D. Hopwoodii*. The reaction was strongly alkaline.

In another paper, dated September, 1879, the above account is confirmed(29). Von Mueller says: "Piturine is in some respects allied to nicotine, but more closely akin to duboisine (of *D. myoporoides*), the latter being lighter in colour, of bitter, not acrid, taste, and of fainter odour."

In Czapek's text-book—Biochemie der Pflanzen, p.311—the statement occurs that "*Duboisia Hopwoodii* contains 1·1% of an alkaloid, earlier known as piturine, which is identical with hyoscyamine." And again, in Wehmer's text-book—Die Pflanzenstoffe, p.695, the same erroneous statement is found. There is no doubt that the name "duboisine" has been used for the alkaloid of both plants.

ix. About this time, Ladenburg was investigating the constitution of the atropine group of alkaloids, and their relation to one another. After reading the account of Gerrard's work, he concluded that a more accurate chemical investigation was necessary to decide the true nature of duboisine. Since only two strongly midriatic alkaloids were known to occur naturally —atropine and hyoscyamine,– Ladenburg set out to determine whether duboisine was identical with one of these, or a new tropeine alkaloid. This was all the more interesting as "daturine," the alkaloid in *Datura stramonium*, had already been shown to be atropine, by Planta, but was subsequently proved by Ladenburg (**34**) himself to be identical with its isomer hyoscyamine. Ladenburg received from Merck, in 1880, a few grams of duboisia sulphate in the form of a resinous residue. By carefully purifying the gold salt, he finally obtained the very characteristic crystals of gold hyoscyamine, m.p. 159°C.(**33**).

Shortly after this, in 1880, Gerrard (**36**) announced to the Pharmaceutical Society of London that he had succeeded in preparing crystallised duboisine. This he obtained in two different forms by a certain solvent (which he does not mention), and he was unable to say whether these were of the same or different constitution.

In 1882, Gibson (**37**) studied the action of Duboisia on the circulation, and his results showed the typical action of the atropine group.

Professor Harnack(**39**), the pharmacologist, subsequently challenged Ladenburg's statement that duboisine and hyoscyamine are identical, and affirmed that the former was much stronger. Ladenburg (**40**) was accordingly induced to return to the subject, and, in 1887, having obtained a few grams of the commercial

duboisine from Merck, he prepared the gold salt of hyosine, m.p. 197-8°C. The mother-liquor yielded no other alkaloid, so that this time no hyoscyamine was present. The author attributed the different results to variations in the method of manufacture.

Shortly afterwards (1890), Messrs. Schering and Co. (41) treated a quantity of the leaves of *D. myoporoides* for alkaloid, and obtained the sulphate of a base showing identical properties with hyoscyamine sulphate, while, from the mother-liquor, hyoscine was obtained.

According to Schmidt (42) and Merck, Ladenburg's hyoscine, which he discovered in the henbane in 1880 and in Duboisia in 1887, was identical with scopolamine, and Schmidt identified his scopolamine in small quantities in the leaves of *D. myoporoides* in 1888. The next account is that of Bender, who obtained samples of the leaves from two different sources. He obtained scopolamine in one, and hyoscyamine in the other. Bender brought his samples to Schmidt, who immediately confirmed these results. Schmidt (42) also obtained, at this time, large quantities of leaves from Schuchart, of Görlitz. He prepared the gold salt, and could find no hyoscyamine or atropine, but only the brilliant, serrated needles of the salt of inactive scopolamine (m.p. 208°C.). Schmidt here states that the previous assumption of Ladenburg is incorrect, but the variation is due to the fact that duboisia leaves of commerce sometimes contain one and sometimes the other base.

x. In 1892, E. Merck (45) discovered in *D. myoporoides* a new midriatic alkaloid which he named pseudo-hyoscyamine. He identified the bases scopolamine and hyoscyamine, and showed that the new base was different from these (m.p. of gold salt, 176°C.). He also stated that the analytical data suggested the probability that the gold salt contained an admixture of still another base with lower molecular weight.

In the large quantities of uncrystallisable aurichloride residues, Merck recognised considerable amounts of amorphous bases which contained none of the alkaloids mentioned.

xi. In 1895, Dr. Lauterer (47), of Brisbane, gave an account of some tests on the alkaloids which he extracted from this

plant. He found, by Gerrard's colour-test with mercuric chloride solution, that hyoscyamine alone was present in old leaves and twigs, but that the fresh young leaves contained mostly scopolamine.

From this period, the chemistry of Duboisia was neglected for seventeen years, till, in 1912, the Wellcome Research laboratories received a large supply of the plant from the Philippine Islands. Carr and Reynolds (**50**) obtained from this material 1·1% of hyoscyamine and 0·15% of pseudo-hyoscyamine. The latter alkaloid was found by them to possess the constitution of nor-hyoscyamine, but they detected no scopolamine in this material.

Duboisia Hopwoodii F.v.M.

xii. The poisonous principle of the "pituri" plant was studied by medical specialists in Great Britain in 1878, and the chemist Gerrard(**7**) found an alkaloid present which he named "piturine." In 1879, Petit, of Paris (**11**), showed that the alkaloid was nicotine. In 1880, Professor Liversidge revised the analytical work, and obtained a formula for the alkaloid, of lower molecular weight than nicotine: the difference lay in the determination of the nitrogen. It stood thus doubtfully as a new alkaloid under the name of "piturine" for thirty years. Petit's results were recently confirmed by the late Dr. Rothera, of Melbourne (**15**), and the base has been shown to be identical with nicotine in its chemical, physical, and pharmacological properties. Hartwich(**14**) in 1910, and Senft (**16**) in 1911, wrote good descriptive accounts of the plant, including the histology of the leaves and stems, and showing a number of sections. Hartwich compares the histology of the two species. In both accounts, the chemical data show all the positive reactions of nicotine, although the alkaloid is referred to as "piturin." Senft obtained his pituri and information from two Austrian scientists, Domin and Danes, who visited Australia in 1910. All these were unacquainted with Rothera's results. This plant is a shrub or small tree growing to an average height of about eight feet. It is found only in the interior of the continent; it crosses the border on the east

into New South Wales and Queensland; and, on the other side, it extends into Western Australia almost to the centre of that State (J. H. Maiden).

Critical Review of the Chemistry of the Duboisias.

xiii. The earlier investigators of the Duboisias were apparently impressed by the very great similarity in the general appearance and morphology of the two species. This is evident in their methods of working as well as in their manner of writing; and one sees in their chemical investigations that they suspected the poisonous principles, too, would be found similar in nature. Accordingly, we find it stated that Staiger first isolated the two *volatile* alkaloids "piturine and duboisine." An alkaloid was prepared from *D. myoporoides* by von Mueller and Rummel, in the same way as nicotine from tobacco. It was a volatile, oily, liquid alkaloid, having a strong odour of tobacco, and was considered as probably identical with piturine. Branches of *D. myoporoides* hung up in a close room produced giddiness and vomiting. Von Mueller and Rummel described the alkaloid obtained by them from *Duboisia Hopwoodii* (pituri) under the name "Duboisine" (10).

On the other hand, the more recent investigations show that *D. myoporoides* contains only the non-volatile alkaloids of the atropine group.

One can only conclude from this conflicting evidence regarding the nature of the active principles, that the earlier workers obtained in their researches, certain incomplete results which were wrongly interpreted by them, and that some authors confused the two plants, or were unaware of the existence of two Duboisias.

A few experiments are now described, which were suggested by the above statements, chiefly to decide the question as to whether in *D. myoporoides* there is present any volatile active principle.

Experimental.

xiv. *Method:*—Fresh plants of *D. myoporoides* were ("treated in the same way as for the extraction of nicotine from tobacco")

crushed, and placed in a distillation flask fitted with a spray-trap. Lime or soda in excess was added, and the whole mass distilled in a current of steam for five or six hours. The ammoniacal distillate was neutralised with acid and concentrated on the water-bath to small volume. The remaining fluid was shaken out, first with ether in presence of acid, then with chloroform after making alkaline. The chloroform was carefully washed and dried, and distilled to remove the solvent. The residue was then weighed and titrated.

Material was obtained from the Sydney Botanic Gardens, the National Park, the North Coast district of New South Wales, and from Queensland. The plants were collected at different seasons throughout the year.

Results :—The ether extracts contained a volatile essential oil of most disagreeable odour.

From eleven separate distillations of the above material, there was obtained, on evaporating the chloroform extract, a small residue, which contained alkaloid in every case. The amounts roughly correspond to 1-2 mgs. per hour of distillation.

xv. *Composition of the volatilised substance :*—

(a) Titration, with centinormal solutions and iodeosin indicator, showed that each of these residues left on evaporation of the chloroform, consisted of about half its weight of an alkaloid.

(b) The residues were yellowish-brown syrups. They were dissolved in a little acidulated water, and the following tests applied. The solutions possessed an intensely bitter taste, and alkaline reaction to litmus.

(c) The general reagents for alkaloids, viz., Wagner's, Mayer's, and Sonnenschein's solutions, picric, tannic, and phospho-tungstic acids all gave dense precipitates with the solution. The substance, therefore, contained an alkaloid.

(d) The specific tests for the identification of the known volatile alkaloids, such as nicotine, in all cases gave negative results.

(e) Vitali's test gave a brilliant red colour, which indicated the presence of an alkaloid of the atropine group.

(f) The solution was diluted to 1 part of residue in 500 normal saline (1 in 1000 alkaloid), and when one drop of this was instilled into the eye of a dog, wide dilatation was produced in about 20 minutes. The alkaloid was therefore of the midriatic group.

Evidence was thus obtained from these results that the alkaloids assumed to be non-volatile, had distilled over in small quantities, under the conditions stated. The next step, therefore, was to ascertain the behaviour of pure atropine, when treated in the same way.

xvi. *Control experiment.—Method :*—Pure atropine sulphate solutions with excess of lime, with and without sawdust, were distilled in a current of steam, from a flask fitted with a Kjeldahl spray-trap. At the end of each hour, the distillate which reacted alkaline to litmus, was shaken out with chloroform. The chloroform extract was then washed and dried, and the solvent distilled off. The residues were weighed and titrated, and afterwards examined.

Results :—Very erratic results were obtained. In some, the amount of residue decreased to nothing in the five successive hours. In others, they varied much, even increasing at the end. In general, a total weight of 20 mgs. was obtained after five hours. This yield was apparently independent of the amount of alkaloid taken, which was between 0·1 and 1·0 mg. The addition of sawdust did not alter the result. All the residues contained alkaloid.

When a distillate, without previous neutralisation, was evaporated in an open basin over a bunsen flame, the residue contained only a trace of alkaloid.

(a) By titration of these residues as in the previous series, the amount of alkaloid (as atropine) in five hours' distillation was 11 mgs. If the latter be taken as representing the actual amount of alkaloid in each total distillate, then the alkaloid has distilled over under the conditions of these experiments at a rate of 2 mgs. per hour. From these titrated solutions, the alkaloid was recovered and examined.

(b) The aqueous solution, faintly acidulated, possessed a very bitter taste, and alkaline reaction to litmus.

(c) Dense precipitates were obtained with all the general alkaloid reagents.

(e) On applying Vitali's test for atropine, a deep red colour was shown.

(f) The solution was brought to 1 in 1000 with normal saline, and one drop of this instilled into the eye of a dog. Almost complete dilatation was produced within 30 minutes.

The distillate therefore contained atropine, and the results showed that when solutions of atropine are distilled in a current of steam, the alkaloid volatilises. Also, when very dilute solutions of atropine are evaporated by boiling in an open basin, the alkaloid may be almost entirely lost.

Application of the results.

xvii. *The Statement.*—The foregoing experiments afford conclusive evidence that, when leaves of *Duboisia myoporoides* were distilled with alkali in a current of steam, an alkaloid volatilised and was obtained in the distillate. This alkaloid was a minute proportion of the atropine and hyoscyamine, which are known to be present in the leaves, and which have always been assumed to be non-volatile.

When solutions of pure atropine were distilled in the same apparatus, and under the same conditions, atropine distilled over, and almost at the same rate as from the plant, 1-2 mgs. per hour.

The Interpretation.—We are now enabled by these results to interpret some of the contradictory statements of the earlier investigators. *D. Hopwoodii*, the first to be examined chemically, had yielded nicotine, and from the closely related *D. myoporoides* an alkaloid was obtained in the same way as nicotine. In the extraction of the midriatic alkaloids, even with modern improvements, the crude product first obtained is invariably a viscous, oily liquid, or syrupy residue. One must not, however, assume that it contains any of the liquid alkaloids, such as nicotine, since the residue will eventually crystallise when properly puri-

fied. Even pure atropine, when dissolved in chloroform, alcohol, or water, and the solution evaporated on the water-bath, is left as a syrupy residue. If these viscous semi-fluid residues be distilled, as described, the distillates will yield all the tests for the alkaloid, and so the isolation of the "volatile, liquid alkaloids, piturine and duboisine," is explained.

The early experimenters were thrown off the track again, in their attempt to solve this difficult problem, by another factor—the "strong odour of tobacco." This is stated frequently in the literature, and no doubt played a large part in setting the bias towards nicotine. During the chemical investigation of many other solanaceous plants, especially Solandra, the Solanums, and Nicotiana species, the author has noted the strong odour which makes itself prominent at certain stages It is particularly strong when a solution is evaporated to dryness, and when the chloroform is distilled off from the last extract; and a syrupy residue is left, which contains the crude alkaloids. This residue, in all the cases just mentioned, possessed this peculiar odour—powerful, nauseous, and disagreeable. It somewhat resembles very stale nicotine or conine, but is due to a volatile essential oil which is probably present in all these plants. It was isolated from the steam-distillates previously described, by acidulating and shaking out with ether. When the ether was slowly removed at air-temperature, the residue exhibited all the objectional properties described. This residue gave no alkaloidal reactions.

It is thus shown that the statements "a volatile, liquid alkaloid possessing the odour of tobacco," and "consisting of atropine or hyoscyamine," are both correct, and in accordance with experimental facts.

"Duboisine."

xviii. The chemical history of the midriatic alkaloids, which have been isolated from *Duboisia myoporoides*, possesses peculiar interest and importance. "Duboisine," the commercial crude drug, is still extracted, and is found in commerce as the total mixed alkaloids. In 1912, Merck's pure crystallised duboisine

cost £10 per oz., and its salts, including the sulphate, £5 per oz. In 1916, British catalogues contain duboisine sulphate at £25 per oz. Its use is almost entirely confined to ophthalmic work, and as each of these alkaloids is powerfully midriatic, a variation in the composition of the mixture affects but little the main result. This is in marked contrast to the action on the central nervous system, where hyoscyamine acts as a stimulant, and scopolamine as a depressant and hypnotic. The relative midriatic values are given as :—

Scopolamine	... 20	(Bastedo's Mat. Med., 384).
Lævo-hyoscyamine	16	(Cushny).
Atropine...	... 8	(Wynter Blyth's Poisons, 384).
Nor-hyoscyamine..	2	(Carr and Reynolds, J.C.S. 1912, 948).
Nor-atropine	... 1	„ „

Before 1880, duboisine was recognised as closely resembling, but not identical with atropine.

In 1880, Ladenburg found it to be entirely hyoscyamine. Harnack emphasised that it was much stronger.

In 1887, Ladenburg isolated only scopolamine, no other being present.

In 1890, Schering and Co. separated both hyoscyamine and scopolamine.

In 1891, Bender obtained from one sample of leaves only hyoscyamine, and from another different sample only scopolamine. Schmidt repeated and confirmed Bender's results.

In 1892, Schmidt obtained inactive scopolamine only. Merck obtained pseudo-hyoscyamine, hyoscyamine, and scopolamine.

In 1912, Carr and Reynolds separated nor-hyoscyamine (Merck's pseudo-h.) and hyoscyamine only, no scopolamine being present.

In 1916, the writer examined an old sample of commercial duboisine purchased from Messrs. Baird and Tatlock, of London. He isolated from the gold salts a fraction with the melting-point of lævo-scopolamine, a second fraction containing nor-hyoscyamine, and a third containing lævo-hyoscyamine. A considerable proportion of the alkaloids separated as viscous particles on further concentration of the mother-liquors.

How are these variations to be explained? Ladenburg has stated that they were due to different methods of manufacture, but he believed that his hyoscine was a true isomer of hyoscyamine, and therefore his opinion was legitimate. We are now certain that these two bases possess a different chemical composition, and therefore cannot be transformed in this way, so that Schmidt's view was nearer the truth—that the leaves sometimes contained hyoscyamine, and at other times scopolamine. Our present biochemical knowledge, however, will scarcely admit of this view, that a plant under variable conditions may alter its fundamental chemical products. But it is quite possible that variations in the conditions of growth influence the relative amount of each of these bases, by stimulating and causing a predominance of one, or by reducing the production of another to a minimum amount. The plants probably contain all the alkaloids in question, and none is entirely absent at any time. The detection of the small amounts of one of these alkaloids in the mixture requires the greatest skill and patience, and in most of the papers cited the authors omit the details of manipulation by which alone the value of their results can be estimated.

This example of the variation of the tropeines in the Duboisia is analogous to that of the cocaines in Erythroxylon, and to the strychnine and brucine in the Strychnos plants.

Chemical composition compared.

xix. The two Duboisias, whose history we have been tracing, are thus shown to contain the widely different active principles, nicotine and hyoscyamine, while the original botanical descriptions of the two plants have much in common.

In order to bring out any further points of interest in the comparison of these two plants, a complete chemical analysis of the proximate constituents was made.

In each case, the air-dried leaves were submitted to successive extractions with organic solvents, and the extracts further analysed. The results of these analyses are given in the accompanying table.

	(1) Air-dried leaves.			(2) Dried at 100°C. ash-free.			(3) Fresh leaves.
	D. Hop. woodii.	*D. myopo-roides.*	*D. Leich-hardtii.*	*D. Hop. woodii.*	*D. myopo-roides.*	*D. Leich-hardtii.*	*D. myopo-roides.*
Water lost at 100°C., less volatile constituents	8·10%	10·8%	10·53%	—	—	—	79·48%
Crude ash	18·35	8·0	6·40	—	—	—	1·84
Organic portion (by difference)	73·55	81·2	83·07	100·	100·	100·	18·68
Extracted by petroleum spirit	6·63	4·90	2·72	9·01	6·04	3·28	1·13
Volatile oils	0·70	0·08	0·24	0·95	0·10	0·29	0·02
Fatty oils	4·88	4·30	1·30	6·63	5·30	1·57	0·99
Resins	1·00	0·52	1·18	1·36	0·64	1·42	0·12
Alkaloid	0·05	—	—	0·07	—	—	—
Extracted by ether	2·82	5·21	3·61	3·83	6·42	4·35	1·20
Water-soluble:—organic acids, etc.	0·55	0·31	0·20	0·75	0·38	0·24	0·07
Alkaloid	0·02	trace	—	0·03	trace	—	trace
Alcohol-soluble:—resins, chlorophyll	2·25	3·49	2·73	3.05	4·30	3·29	0·80
Alcohol-insoluble resins	trace	1·41	0·68	—	1·74	0·82	0·33
Extracted by alcohol	13·15	3·750	4·220	17·86	5·480	5·08	0·86
Water-soluble portion	9·69	3·525	3·182	13·18	—	3·83	—
Tannins	8·76	0·383	0·048	11·90	0·472	0·06	0·09
Acid-ether extract	0·14	0·011	0·066	0·19	0·013	0·08	—
Alkali-chloroform extract—non-alkaloidal	—	0·900	0·936	—	1·105	1·14	0·21
alkaloidal	0·93	0·173	0·411	1·27	0·213	0·50	0·04
Water-insoluble portion	3·46	0·575	1·038	4·68	0·708	1·25	0·13
Tannin decomposition-products—soluble in ammonia	—	0·500	0·055	—	0·616	0·07	0·11
Alcohol-soluble resins	—	0·070	0·750	—	0·086	0·90	0·02
Alcohol-insoluble resins	—	0·005	0·233	—	0·006	0·28	—
Extracted by water	13·62	11·29	8·71	18·51	13·06	10·49	2·59
Mucilage	4·92	1·86	1·04	6·69	2·29	1·25	0·43
Glucose	4·09	1·00	—	5·56	1·23	small	0·23
Saccharose	1·06	1·00	0·06	1·44	1·23	0·07	0·23
Total extracted by solvents	36·22	25·15	19·26	49·21	31·00	23·20	5·78
Cellulose, lignin, etc. (by difference)	37·33	56·05	63·81	50·79	69·00	76·80	12·90
Total organic portion	73·55	81·20	83·07	100·00	100·00	100·00	18·68

The *Duboisia Hopwoodii* was part of a stock in the possession of Sir Thomas Anderson Stuart, to whose kindness the author is much indebted. After its long journey from the interior, the pituri plant is received in the form of very dry leaf-fragments mixed with broken stalks and twigs. The leaf-portion, constituting 50% of the whole, was carefully separated from the sample, and finely powdered for the analysis.

The *Duboisia myoporoides* was collected in the National Park by the kind permission of the Trustees. The leaves were taken from trees about 25 feet high and at the time of flowering.

The *Duboisia Leichhardtii* F.v.M., is a third species, whose chemical composition is yet unknown. It was collected by the author, near the Stuart River in Queensland, at the same time of year as in the preceding specimen, and while in flower.

The total alkaloids in each plant were also estimated, and the results are given in the accompanying table.

The author desires to express his thanks to Sir Thomas Anderson Stuart for laboratory facilities afforded during this investigation.

AMOUNT OF TOTAL ALKALOIDS.

	Air-dried.	Dried at 100°, ash-free.	Fresh.
Duboisia Hopwoodii, leaves ..	1·00%	1·36%	0·27%
D. Leichhardtii, leaves	1·28	1·42	0·28
D. myoporoides, mature leaves ...	0·17	0·21	0·04
D. myoporoides, seedling leaves ...	0·073	0·082	0·017
D. myoporoides, bark	...	0·027	...

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THE CHEMICAL INVESTIGATION OF SOME POISONOUS PLANTS IN THE N.O. SOLANACEÆ.

Part v.—The Alkaloids of *Duboisia Leichhardtii* F.v.M.

By James M. Petrie, D.Sc., F.I.C., Linnean Macleay Fellow of the Society in Biochemistry.

(From the Physiological Laboratory of the University of Sydney.)

[Issued 11th July, 1917.]

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Duboisia Leichhardtii is a small evergreen tree, endemic in Eastern Australia. It was discovered by Leichhardt in his travels, and sent by him to Baron von Mueller, who described it in 1867. Leichhardt's specimens are in the Melbourne Herbarium, but no locality is given other than "extra-tropical Eastern Australia." The first specimens bearing a definite locality were obtained from Mt. Playfair, near Springsure in Central Queensland. These were sent by a squatter to von Mueller in 1890, and are also in the Melbourne Herbarium. In the same year, it was found by Dr. J. Shirley growing along the Stuart River, 140 miles north-north-west of Brisbane, and specimens were placed in the Queensland National Herbarium. The only other record of this plant is that in Moore and Betche's Flora of New South Wales, where it is stated to have been found in the Gray Ranges, which cross the extreme north-west corner of New South Wales into Queensland. But there are no corresponding specimens from this locality in Australian collections.

Though so very little is known, and the records are so few, concerning *Duboisia Leichhardtii*, the three localities given lie in a great inverted crescent, 800 miles long, stretching across Queensland from the south-west corner, through the central area, and down to the south-east.

Von Mueller described the plant under the name of Anthocercis, in his Fragmenta phytographia (Vol. vi., 1867-8, p.142),

and ten years later the name was transferred to Duboisia (Wing's Southern Science Record, ii., 1882, 222). Of the three described species of Duboisia, *D. Hopwoodii* is confined to central Australia, *D. myoporoides* extends along the eastern coastline, and *D. Leichhardtii* apparently occupies the intervening country, which joins up the areas occupied by the other two species.

Although in their essential features they exhibit fundamental differences which characterise them as distinct species, they possess a peculiar similarity in their general aspect, and the writer, familiar with the species *D. myoporoides* only, had no difficulty in recognising *D. Leichhardtii* when first seen in the forests of central Queensland. In some respects *D. Leichhardtii* may be regarded as intermediate between the other two, for example, in the average heights of adult trees—*D. Hopwoodii* 8 feet, *D. Leichhardtii* 15 feet, and *D. myoporoides* 25 feet; or in the relative sizes of their mature leaves—2, 3, and 4 inches in length respectively. On the other hand, in comparing the details of the original botanical descriptions, one can hardly say that *D. Leichhardtii* inclines towards one or the other species. It is differentiated chiefly by the flowers possessing long, acute corolla-lobes. Much interest was aroused by the speculation as to whether, in regard to its active principle, this third species would resemble *D. Hopwoodii* or *D. myoporoides*, or differ from both. We have seen (Part iv. of this series) that *D. Hopwoodii*, the pituri plant, contains nicotine, and that *D. myoporoides*, the cork-tree, contains hyoscyamine and nor-hyoscyamine. This point was soon settled, but only after the completion of the investigation, a casual reference was found in a Medical Journal, to an account of some tests by Lauterer, of Brisbane, (Aust. Med. Gaz., xiv., 1895, 457) which he made on the alkaloids of *Duboisia myoporoides*. He states that, in this plant, he found hyoscyamine and scopolamine, and that "*D. Leichhardtii* contains mostly scopolamine." With the exception of this statement of a single line, no other information has been found regarding the chemical constituents. It is doubtful whether Lauterer ever worked on *D. Leichhardtii* at all; if he did, it was wholly unknown to his

friends of the Royal Society of Queensland (private communication from Dr. J. Shirley).

The results which Lauterer entirely depended upon for his conclusion in the case of *D. myoporoides* were obtained from qualitative tests only, and chiefly Gerrard's mercuric chloride reaction. The author, in repeating these tests with pure alkaloids, obtained results which did not agree with the statements of Gerrard (Pharm. Journ., xxi., 1891, 898). For instance, pure atropine and hyoscyamine were dissolved in chloroform and evaporated on a watch-glass. A 2 per cent. solution of mercuric chloride in 50 per cent. alcohol was then added drop by drop, when a yellow precipitate was obtained in both cases. These remained yellow for some hours, though they became red on heating. Atropine is stated by Gerrard to be distinguished from hyoscyamine by giving a red colour at once, without heat. Scopolamine was found to give a white precipitate, and nor-hyoscyamine also gave a white precipitate when tested in the same manner. In this way certainly hyoscyamine may be distinguished from scopolamine when separate; but, in a mixture of alkaloids, the observation of a white precipitate in Gerrard's reaction does not justify the conclusion that only scopolamine is present. The author obtained a white precipitate in the mixture of alkaloids obtained from *Solandra longiflora* (Part iii. of this series) in which no scopolamine was found, but which contained hyoscyamine, nor-hyoscyamine, and atropine.

Source of the Material.

The material for this investigation was collected in Queensland by the author, accompanied by Mr. C. White, Assistant Government Botanist. The starting point for the Duboisia country was the North-West Railway terminus at Nanango, and directions had been obtained from Dr. Shirley, who discovered the trees in this region in 1890. Far up the Stuart River and about 10 miles from Taabinga cattle-station, the first specimens of *D. Leichhardtii* were seen; and after two days' driving through open forest-country, they were still observed stretching away to the south-west towards the Bunya Bunya Mountains.

As far as can be ascertained, they are not found south of the mountains which form the watershed of the Brisbane Valley.

The trees were always observed in small clusters, growing on red volcanic soil, and only on the edge of the thin scrubs in the open brush forests.

They were invariably associated with certain prominent ironbark and acacia trees, among which the following species were noted:—*Eucalyptus crebra* (narrow-leaved ironbark), *E. paniculata* (white ironbark), *E. melanophloia* (silver-leaved ironbark), *E. tereticornis* (red gum), *E. hemiphloia* (gum-top box); *Angophora lanceolata* and *A. subvelutina*. Among the acacias were *A. penninervis*, *A. Cunninghamii*, *A. implexa*, a variety of *A. decurrens*, and *A. aulacocarpa*.

Experimental.

(i.) *Preliminary Examination for Alkaloids:*—A small quantity of the material was extracted in a Soxhlet extraction-apparatus and treated by the Stas-Otto process for the separation of active principles. A substance was obtained which gave positive reactions with the following reagents:—Iodine in potassium iodide, potassium mercuric iodide, phosphomolybdic, picric, tannic, and phosphotungstic acids, platinic and auric chlorides.

The solution possessed an intensely bitter taste and alkaline reaction.

When diluted to 1 in 1000 with normal saline and instilled into the eye of a dog, wide dilatation was produced in about 30 minutes.

It gave a strong positive reaction with Vitali's test.

The substance is thus shown to be an alkaloid of the atropine group; and since the aurichloride salts were observed under the microscope to consist of several kinds of crystals, the probability is that they contain a mixture of associated alkaloids of the midriatic group.

(2.) *Distillation for Volatile Constituents:*—About 100 gms. of air-dried leaves were powdered and mixed with milk of lime in a large flask. The mass was distilled in a current of steam

for seven hours. The alkaline distillate was shaken out with ether, and this ethereal liquid, after separating and drying, was distilled at a low temperature to dryness. This residue was dissolved in water and titrated, when it required 23 ccs. of centi-normal acid to neutralise. The fluid was then acidified and shaken out with ether, when about 11 mgs. of an oily substance were separated. On making faintly alkaline with ammonia and agitating with chloroform, a substance was removed which was afterwards obtained as a viscous residue. This weighed about 55 mgs., which is equivalent to 8 mgs. per hour. It gave precipitates with all the alkaloidal reagents, and also the characteristic Vitali's reaction for the atropine group; while a solution in normal saline 1 in 1000, widely dilated the eye of a dog in about 20 minutes.

It is apparent from these results that a minute quantity of the atropine alkaloids has distilled over, as has already been proved by the author to take place with other plants containing alkaloids of this group (Part iv. of this series).

(3.) *Extraction of the Alkaloids:*—The air-dried leaves containing 9·7 per cent. of water were ground to a fine powder, and extracted with cold methylated spirit. At weekly intervals, the latter was removed until only traces of alkaloid were dissolved. The voluminous alcoholic extracts, obtained by draining and pressing the material, were distilled under reduced pressure, and below 60°C., when there remained a dark-coloured viscous residue. This was removed by washing with successive small quantities of warm water slightly acidulated, and filtered. For the removal of colouring matter and resins, this dark brown fluid was next treated with lead acetate. The lead precipitate was carefully washed free from alkaloid, and the aqueous fluid and washings freed from lead. The solution, now only slightly coloured, was concentrated at 60°C. to a small volume. Wagner's iodine reagent was then used to precipitate the alkaloids. This iodine precipitate was decomposed by sulphurous acid, and the solution was shaken out with ether. This solvent removed a considerable amount of impurity. The aqueous solution was next made

alkaline with a very slight excess of ammonia, which separated the alkaloids in a dense white precipitate. The alkaloids were then removed in solution by agitating repeatedly with equal volumes of chloroform. The chloroform was removed by distilling under diminished pressure, when there was left in the flask a semi-solid mass, which, after standing some days, crystallised in beautiful white radiating needles.

The original plant-material was not treated in one large bulk, but in a number of small portions as required. In one of these, which yielded the maximum weight of alkaloids, the following data were recorded:—300 gms. of air-dried plant extracted for 24 days altogether. The aqueous extract was concentrated to 350 c.cs., and precipitated with one litre of Wagner's decinormal iodine solution. Ether removed from this acid solution about 2 gms. of impurities, and chloroform from the alkaline liquid yielded 5 gms. of crude alkaloid. A portion of the latter in solution was titrated with decinormal acid and iodeosin indicator, and the result showed that 81 per cent. consisted of pure alkaloid. The yield was, therefore, 1·42 per cent. of alkaloids in the dried (at 100°C.) plant-leaves, or 0·28 per cent. in the fresh plant.

The optical activity of a solution of this crude alkaloid in 50 per cent. alcohol was determined, $[\alpha]_D$ —18°.

(4.) *Separation of the Alkaloids*:—The mixed alkaloids were converted directly into aurichlorides, by the addition of gold chloride to the solution of alkaloids in dilute hydrochloric acid. The yellow precipitate was dissolved in sufficient warm water, and set aside to slowly crystallise spontaneously. At regular intervals, the crystals were removed by decanting the superfluid. These crystals were washed and the melting-points determined, then redissolved in dilute hydrochloric acid and again set aside to crystallise. After a long and tedious process of fractional crystallisation, the various fractions being placed together, or separated, according to their melting-points, the latter were observed to concentrate near certain definite temperatures. These fractions were finally obtained with melting-points which did not change after further recrystallisation. A summary is

given in the following table of only the principal stages in the separation of these salts.

Fractional Crystallisation of the Aurichloride Salts.

a { 1. Brown viscous deposit.
2. Yellow crystals, m.p. 135-178°.
3. Amorphous yellow mass.

b { a1 was washed and found to be non-alkaloidal.
a2 was recrystallised.
a3 was decomposed and the alkaloids recovered by shaking out with chloroform. The gold salts were then reformed and crystallised.

c { (a2+a3) when recrystallised gave (1) yellow crystals, m.p. 174-179°
(2) ,, ,, 136-162
(3) ,, ,, 180-190
(4) uncrystallisable portion.

d { c1 when dissolved and recrystallised yielded 1. 177-179° 2. 135 small amt.
c2 ,, ,, ,, 3. 165-167 greater part. 4. 135-150
c3 ,, ,, ,, 5. 197-199 greater part. 6. 186

e { d1 when dissolved and recrystallised yielded (1) 178, 179, 179°
d3 ,, ,, ,, (2) 165-166
d2+d4 ,, ,, ,, (3) 137, 137
d5 ,, ,, ,, (4) 198, 198, 197

f { e1 when dissolved and recrystallised yielded 179, 179, 179°
e2 ,, ,, ,, 165-166
e3 ,, ,, ,, 137, 136, 137
e4 ,, ,, ,, 197-198

(5.) *Identification of the Alkaloids.*—The most recent work on the fractional crystallisation of the midriatic alkaloids is that of Carr and Reynolds (J.C.S., ci., 1912, 950). These authors give the following figures for the melting-points of the salts of the pure alkaloids:—

Atropine aurichloride ...	... m.p.137-139°
Lævo-hyoscyamine aurichloride	... m.p.165°
Nor-hyoscyamine ,,	... m.p.178-179°
Lævo-scopolamine ,,	... m.p.198°

A portion of the pure aurichloride crystals thus obtained were then converted into picrates, by boiling their solutions with

sulphurous acid, filtering off the deposit of metallic gold, and treating with a saturated solution of picric acid. These were allowed to stand, the crystals were separated, recrystallised, washed and dried, and their melting points taken.

(1.)	Aurichloride	m.p.179°C.	yields	picrate	with	m.p.219-220°C.
(2.)	,,	165	,,	,,	,,	163-166
(3.)	,,	136	,,	,,	,,	176
(4.)	,,	197	,,	,,	,,	180

The above authorities have given the melting points of the picrates of the pure alkaloids as follows:—

Atropine picrate... ...	... m.p.175-176°C.
Lævo-hyoscyamine picrate	... m.p.165
Nor-hyoscyamine ,,	... m.p.220
Lævo-scopolamine ,,	... m.p.180-181

From one gram of the crude alkaloid there was obtained 0·5 gm. of crystals of the gold salts. This quantity at the end of the fractional crystallisation yielded approximately 0·1 gm. of scopolamine salt, 0·1 gm. of nor-hyoscyamine salt, and 0·2 gm. of lævo-hyoscyamine salt. In other experiments, larger amounts were obtained, but considerable proportions of a viscous uncrystallisable substance always separated.

In the initial stages of the above crystallisation process (a, b, and c), when the crystals had been separated as much as possible, the mother-liquors deposited yellow, amorphous, sticky particles. When the solution was gently warmed, the amorphous substance melted and floated on the surface like oily drops. This portion, which contained part of the alkaloids, could not be induced to crystallise, and further attempts to purify it did not alter its viscous nature.

Summary.

The leaves of *Duboisia Leichhardtii* contain a mixture of the midriatic alkaloids, amounting to 1·4 per cent. of the dried (at 100°C.) material or 0·28 per cent. of the fresh plant. By the fractional crystallisation of their aurichlorides, the mixed alkaloids were separated into nor-hyoscyamine, lævo-hyoscyamine,

lævo-scopolamine, and small amounts of atropine and nor-atropine. These were identified by the melting points of their gold salts and of the picrates.

D. Leichhardtii, therefore, closely resembles *D. myoporoides* in its alkaloids, and these two species are in marked contrast to the only other species known—*D. Hopwoodii*, the pituri-plant, which contains nicotine.

The thanks of the author are due to Sir Thomas Anderson Stuart, in whose laboratory this work was carried out.

Notes taken at National Herbarium

Sydney Botanic Gardens.

(Information supplied by Mr.Cheel.)

Pituri; source:- Duboisia Hopwoodii.

Plant grows in Western Australia, South Australia, Queensland and New South Wales. Western Australian and South Australian broader leaf than the others. Grows on sandstone ridges and in Spinifex country - patchy in distribution - known by many names:- Pituri, Piturie, Pitchery, Pitchiri, Pedgery, Medgery.

Action is narcotic - though some claim it is tonic comparable to strychnine - has been given in debility.

Leaves and small twigs are dried, then wetted with water, mixed generally with the ashes of burnt acacia leaves or those of some other leguminous plant.

Chips, twigs and leaf ends are sometimes burnt and mixed with leaves as above.

The mixture is sometimes filled in green leaves and smoked like a cigar; more usually it is chewed.

Mixture highly prized and is carried about in bags either woven from grass or fibre, or made from skins of animals, fleshy side out (Pituri bags).

On occasions a 'quid' is made for chewing and is passed from one to another - supposed to fill the chewer with goodwill - is offered sometimes to Europeans during such a ceremony.

Notes taken at National Herb

Sydney Botanic Gardens.

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Notes taken at the Sydney

Technological Museum.

PITURI -

Liversidge's source of supply - Barcoo River. Difficulty in procuring sufficient supply for purpose of investigation - blacks will only part with it in very small quantities at a time, - trouble in collecting involves considerable expenditure. Barcoo blacks obtain it from the Diamantina blacks who traded yearly with the Mulligan or Kykockodilla tribe, in whose country the Pituri grows. Collected in the form of broken twigs and fragments of leaves of pale brown colour; odour somewhat similar to tobacco - the fine dust causes sneezing. Western Australian variety much wider leaf than Queensland; South Australian variety. Plant named Duboisia Hopwoodii by Von Mueller - same as that named Duboisia Pituri by Bancroft.

Bancroft states -

The Pituri grows about 50 miles East and West of the boundary between Queensland and South Australia, and from about 22° to 25° South Lattitude. Shrub grows about 8 ft. high - stem at its thickest about 6 inches in diameter. Wood is light, close grained, lemon coloured, with a smell of vanilla when newly cut. Leaves and flowers very similar to Duboisia myoporoides. The fruit - green berry resting in a minute calyx - changes to black as it ripens - contains dark brown kidney shaped seeds covered with minute pits. Ripe berries soon fall off.

Blacks mix the Pituri with the ashes of leaves of a particular plant (acacia) and usually roll the mixture up with a green leaf into the form of a 'quid' before chewing; compare mixing of lime with betel by Malays - probably slowly liberating alkaloid during mastication. On ceremonial occasions quid passed from native to native, finally kept behind original proprietor's ear until required again.

Effects - much the same as those set up by tobacco smoking. Does not appear to have the exciting effect upon the blacks with which it was at one time credited. As is the case with other luxuries it is reserved by the older men for their own use exclusively - neither the women nor the younger men being allowed to use it. Compare smoking and chewing of tobacco by whites. Physiological effect treated by Bancroft. Von Mueller read a paper before the Apothecaries Society of Vienna, probably in 1879, on the chemical actions of the alkaloid. Liversidge's paper treats of the preparation, reaction, composition of the alkaloid and its salts. Ladenburg in 1880 differed from Von Mueller in his conclusions - possibly investigators had different varieties of Duboisia on which they worked.

Notes taken at the Library

Technological Museum.

The Sydney Technological Museum)

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3rd. Edition, page 1015

Notes taken from

The Australian Encyclopaedia.

PITURI

The use of Pituri (pitcheri) as a narcotic is very general. Tribes will send messengers hundreds of miles to obtain by barter the parts of this plant which are prepared for chewing. It produces a voluptuous dreamy sensation. Sometimes it is smoked in pipes. In some parts, at corroborees, the natives produce a condition of frenzy by chewing the leaves of the stinging tree.

JOSEPH BANCROFT (1836-1894)

The investigations of Bancroft into the properties of the Pituri plant led to the discovery of the mydriatic properties of a near relative, Duboisia myoporoides, which have placed its alkaloid, duboisin, in the Pharmacopoeia;

DUBOISIA a genus of the family Solanaceae, consisting of shrubs or trees with small flowers and succulent fruits, D. myoporoides (Corkwood) ranges from New South Wales into Queensland, and extends to New Caledonia. According to Dr. Woolls (quoted by Maiden in "Useful Native Plants") this tree 'has an intoxicating property. The aborigines make holes in the trunk and put some fluid in them, which, when drunk on the following morning, produces stupor. Branches of this shrub are thrown into pools for the purpose of intoxicating the eels and bringing them to the surface.' The timber is white to yellowish, close-grained and firm, though soft when green; it is used for carving and wood-engraving. The bark resembles that of the Cork Oak (Quercus suber) of commerce. D. Hopwoodii, the pituri plant, an inland species, is endemic in Australia. The aborigines of Central Australia masticate its leaves when more or less powdered and mixed with finely broken twigs. So fine is the powder, and so irritating, that when even the most careful handling is accompanied by sneezing. The trees are patchy in distribution, but the blacks travel enormous distances to procure it, and it has become a valuable commodity in tribal barter. The tops and leaves are gathered in August, when the plant is in blossom, and hung up to dry, then packed in netted bags or skins for transport. Sometimes pituri is chewed in company, a quid being passed from one to another. It is also smoked; for this the leaves are damped, mixed with potash prepared from the ashes of plants, and rolled up in the shape of a cigar. In small quantities it has a powerful stimulating effect, assuaging hunger, and enabling long journeys to be made without fatigue, and

The Australian Encyclopaedia.

(Notes from Australian Encyclopaedia)

with little food. The blacks use it to excite them before fighting, and to poison emus. D. Leichhardti is also endemic and limited to the eastern States, chiefly Queensland. Recent investigations show that all three species contain atropine, hyoscyamine and other mydriatic alkaloids.

Notes from "The Arunta" (A study of a Stone Age People)

By

Sir Baldwin Spencer & F.J.Gillen

In some parts the leaves of the pituri plant (Duboisia Hopwoodi, the native name for which is unkulpa), are used to stupefy the emu. The plan adopted is to make a decoction in some small water-hole at which the animal is accustomed to drink. There, hidden by some bush, the native lies quietly in wait. After drinking the water, the bird becomes stupefied, and easily falls a prey to the black fellow's spear.

The leaves and small twigs of the pituri plant (Duboisia Hopwoodi) called by the natives Unkulpa or Ungulpa, are used as a narcotic. They are dried, broken up, packed tightly into woven string bags, each holding two or three pounds weight, and then traded over long distances. Though the plant grows on the sand-hill country around Lake Amadeus and Ayer's Rock, the greater part of that used by the Arunta and neighbouring tribes, such as the Dieri and Urabunna, appears to come from the north-west, in the interior of Queensland, distant at least 200 miles. It is made up into small "plugs", which are passed from mouth to mouth and chewed. When not in use, they are carried behind the ear, or sometimes, in a hole bored through the nasal septum.

The natives describe its making as follows: Unkulpa (pituri) ilpilla (fresh leaf) ka, (alone) alinja (sun) erruma (put them) lumbutchikka (dry) unkulpa (dried leaf) ungnailjilima (grind up) ura (fire) tnimma edunja (native name of Cassia tree) iquincha (ashes) ekinjilla pordiluma (mix them together) kurka quatchilla (a little water) unkulpa inkumella (eat the Unkulpa) pullanja mara oknirra (makes them feel very good or comfortable. That is, - the leaves are dried in the sun; then the twigs of a species of cassia bush are burnt to ashes and the latter pounded up with the Duboisia, mixed with a little water and made into a plug, the chewing of which has a soothing effect.